LEVEL II

AD A102804

Synthesis of Energetic Monomers and Polymers
Annual Progress Report for the Office of Naval Research
Work Request N0001480WR00114 Project RR024-02-01

H. G. Adolph
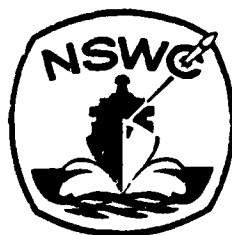
Research and Technology Department

DTIC
AUG 1 3 1981
C

March 1981

DTIC FILE COPY

NSWC

NAVAL SURFACE WEAPONS CENTER

Dahlgren, Virginia 22448 ● Silver Spring, Maryland 20910

81 8 13 012

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
NSWC/MP—81-141	AD H102804	

4. TITLE (and Subtitle)	5. TYPE OF REPORT & PERIOD COVERED
Synthesis of Energetic Monomers and Polymers	Progress Report 1980
	6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)	8. CONTRACT OR GRANT NUMBER(s)
H. G. Adolph	Work Request N0001480WRC0114

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Naval Surface Weapons Center	61153N; 0;
White Oak, Silver Spring, Maryland 20910	0; RR024-02-01

11. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE
	March 31, 1981
	13. NUMBER OF PAGES
	24

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)	15. SECURITY CLASS. (of this report)
	Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Reproduction in whole or in part is permitted for any purpose of the United States Government.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Epoxides; Diols; Polynitro Compounds; Cyclic Formals; Poly formals

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The synthesis of the following energetic monomers was investigated: 2,2,2-Fluorodinitroethoxyoxirane, 3-fluorodinitromethylcaprolactone; glycidyl bis(fluorodinitroethyl)amine. The reaction of fluorodinitromethyl and nitro-substituted diols with formaldehyde and sulfuric acid was studied, and substituent effects on cyclic vs. polyformal formation were elucidated. Efforts to polymerize bis(fluorodinitromethyl)dioxepane and bis(fluorodinitromethyl)dioxocane were mostly unsuccessful.
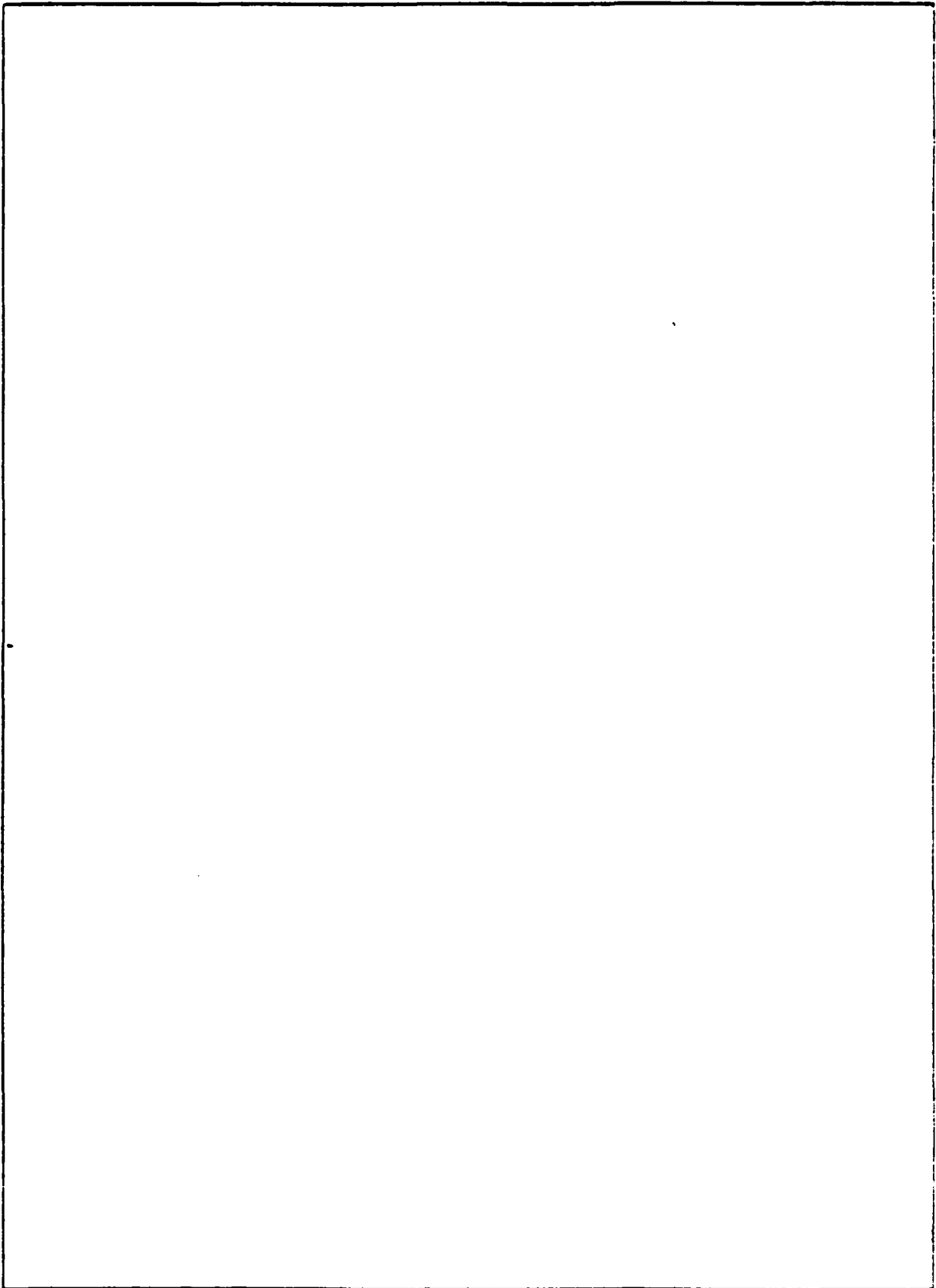
DD FORM 1473 EDITION OF 1 NOV 65 IS OBSOLETE
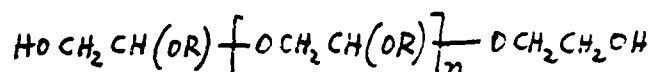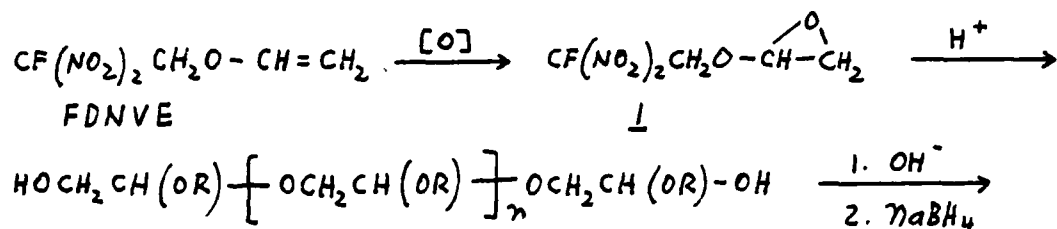1 JAN 73
S/N 0102-014-6601

CONTENTS

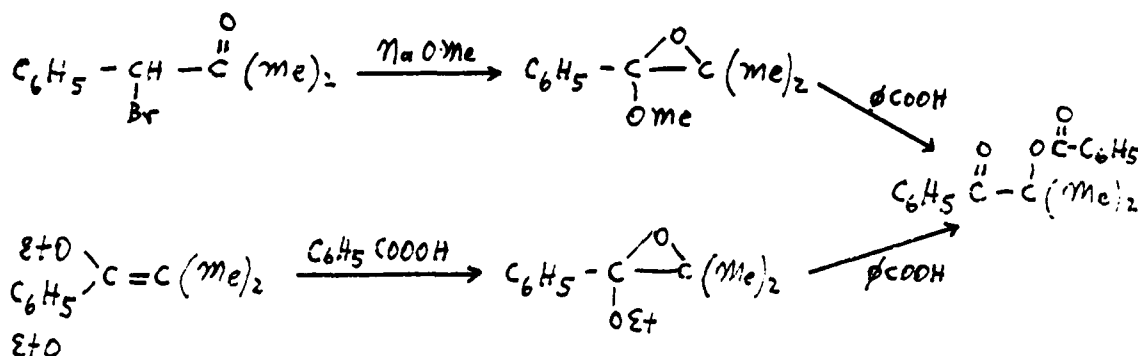## Synthesis of Energetic Monomers and Polymers

Introduction

The objective of this work is the synthesis of new energetic monomers and their conversion to prepolymers with functionality suitable for cross-linking. The preferred functional groups are hydroxy groups which can be reacted with di- and/or triisocyanate, to provide the desired cross-linked polymer matrix for use in plastic-bonded explosives and as propellant binders. During this first year effort several approaches to new monomer structures were evaluated with initial emphasis on the synthesis of fluorodinitro ethoxyoxirane, 1.

Synthesis of fluorodinitroethoxyoxirane, 1.

Fluorodinitroethyl vinyl ether (FDNVE) was prepared several years ago as a potential energetic monomer.[1] However, attempts to polymerize this compound with either cationic or radical catalysts were not successful. In addition the polymer, if it could be prepared, would not have a sufficient number of functional groups for cross-linking. It appeared that oxidation of this vinyl ether to the epoxide would provide an alternative monomer which should be easier to polymerize and give a polymer with the desired functionality after chemical modification of the initially formed end groups.

$$CF(NO_2)_2 CH_2O-CH=CH_2 \xrightarrow{[O]} CF(NO_2)_2 CH_2O-CH-CH_2 \xrightarrow{H^+}$$

FDNVE $\underline{1}$

$$HOCH_2CH(OR)\left[OCH_2CH(OR)\right]_n OCH_2CH(OR)-OH \xrightarrow[2.\ NaBH_4]{1.\ OH^-}$$

$R = CF(NO_2)_2 CH_2$

$$HOCH_2CH(OR)\left[OCH_2CH(OR)\right]_n OCH_2CH_2OH$$

α-Alkoxyoxiranes are not a widely studied class of compounds, but several examples are known.[2,3] Their reported synthesis provide examples for the oxidation of vinyl ethers to α-alkoxyoxiranes.

$$C_6H_5-CH(Br)-C(O)(me)_2 \xrightarrow{NaOme} C_6H_5-C(Ome)-C(me)_2 \xrightarrow{\phi COOH}$$

$$Et O, C_6H_5 \cdot C=C(me)_2 \xrightarrow{C_6H_5 COOOH} C_6H_5-C(OEt)-C(me)_2 \xrightarrow{\phi COOH}$$

$$C_6H_5 \cdot C(O\text{-}C_6H_5)-C(me)_2$$

Similarly, α-acetoxyoxirane was prepared by peracid oxidation of vinyl acetate.[4]

$$CH_3 \overset{O}{\overset{\|}{C}} O - CH = CH_2 \xrightarrow{C_6H_5 \, COOOH} CH_3 \overset{O}{\overset{\|}{C}} O - CH - CH_2$$

The α-alkoxy- and acetoxyoxiranes are readily attacked by acids to give acyloxycarbonyl compounds as indicated above. This reactivity presents a problem in their preparation by peracid oxidation, because the corresponding carboxylic acid is formed as a by-product. Precautions must be taken to prevent the interaction of the oxirane and the acid in the reaction mixture.

FDNVE reacted only slowly with m-chloroperbenzoic acid (MCPBA). In order to minimize contact of m-chlorobenzoic acid with the other reaction product(s) the reaction was run in CCl4 and hexane in which the acid has low solubility. Despite this a mixture of products was obtained from which a single pure compound could not be isolated by distillation or column chromatography. However, the mixture was readily separated by GC as shown in Figure 1.
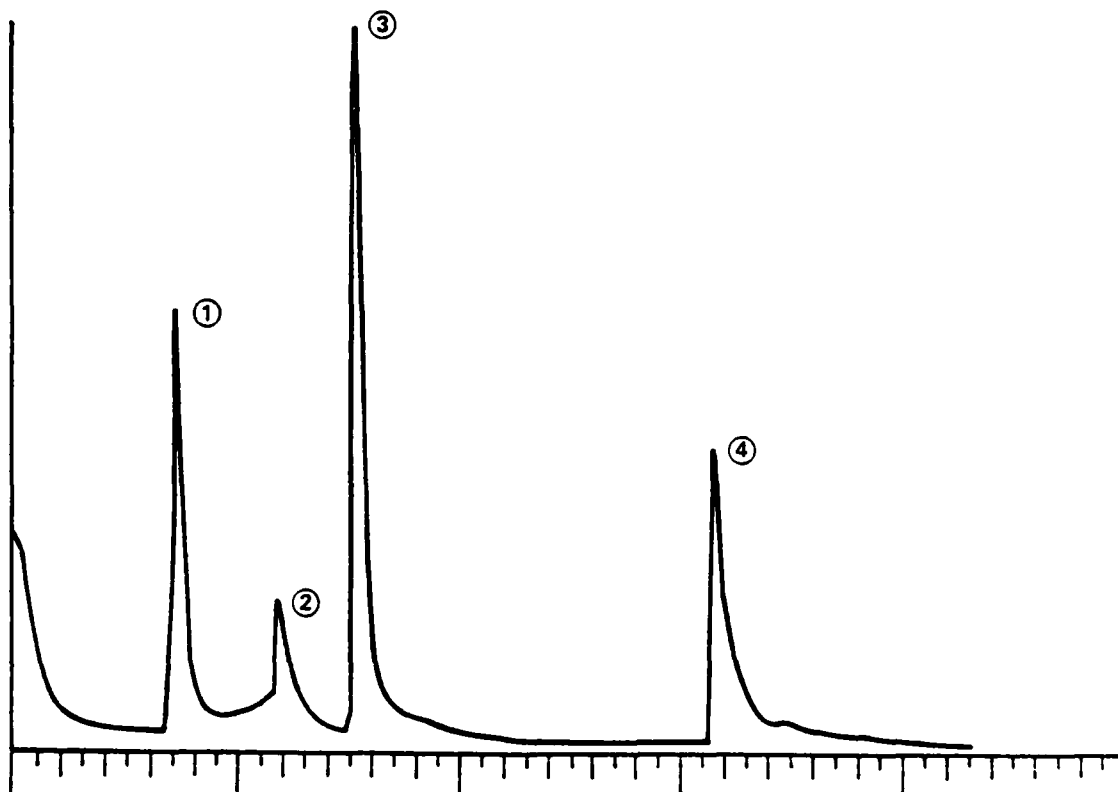

FIGURE 1. GAS-CHROMATOGRAM OF FDNVE OXIDATION PRODUCT

2

It was independently verified that FDNVE does not react with m-chlorobenzoic acid under the reaction conditions used here. Therefore all products must arise from the transformation of an initial product formed from FDNVE and MCPBA. The reaction mixture was successfully analyzed by GC/MS and reasonable structures could be assigned to all products from the mass spectral data obtained with $CI(CH_4)$. The structure assignments are as follows:
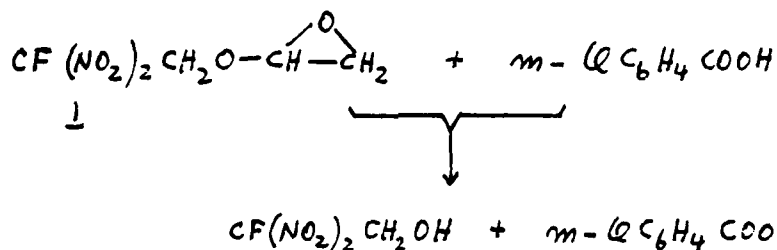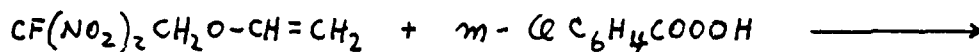
peak 1: FDNVE. Basepeak 181 (M+1); also present 209 (M+29; 4.5%) and 221 (M+41; 0.3%). Major fragments: 155 (M+1 - NO_2); 125 (M+1 - NO - NO_2)

peak 2: Fluorodinitroethanol. Basepeak 125 (M+1 - CH_2O); highest mass 153 (M-1; 10.1%)

peak 3: Fluorodinitroethoxyoxirane, 1. Basepeak 197 (M+1); also present 225 (M+29; 0.5%); 237 (M+41; 0.6%). Major fragments: 167 (M+1 - NO); 155 ($CF(NO_2)_2CH_2OH+1$?) 125 ($CF(NO_2)_2H+1$?)

peak 4: m-Chlorobenzoyloxy acetaldehyde. Basepeak 139 (141) ($m-ClC_6H_5CO$); highest mass 199 (201) (M+1; 7.9 and 2.4%); also present 228 (M+29); 239 (241) (M+41)

This mixture of products is what is expected if the initial reaction products, m-chlorobenzoic acid and 1, undergo further partial reaction according to the scheme observed for other α-alkoxyoxiranes.[2,3]

$$CF(NO_2)_2 CH_2O-CH=CH_2 \ + \ m-Cl\,C_6H_4COOOH \longrightarrow$$

$$CF(NO_2)_2 CH_2O-\overset{O}{\overset{\diagup\diagdown}{CH-CH_2}} \ + \ m-Cl\,C_6H_4\,COOH$$

1

$$CF(NO_2)_2 CH_2OH \ + \ m-Cl\,C_6H_4\,COOCH_2\,CHO$$

Since no m-chlorobenzoic acid was found in the CCl_4-soluble part of the reaction mixture, any of it still present after work-up must have reacted completely with 1. From the reaction in CCl_4, 70% of the theoretical amount of m-chlorobenzoic acid was filtered off as insoluble product. When the crude reaction mixture from the peracid oxidation in CCl_4 was exhaustively extracted with 0.02, then 0.1N NaOH and, after drying, the solvent was removed, a viscous oil remained whose ir spectrum indicated the presence of $CF(NO_2)_2$ as well as a small quantity of $m-ClC_6H_4COO$. It is assumed that this material is a polymer derived from 1.

3

The existence of 1 seems established beyond reasonable doubt, even though it was not isolated in pure form. It is possible that reaction between 1 and carboxylic acid can be minimized further and that pure 1 could be obtained from the reaction used here. This will not be easy because of the long reaction time required and the sensitivity of 1 to bases which prevents easy scavenging of the acid. However, this reaction has not been studied exhaustively and scavenging techniques using diazomethane or immobilized peracid are unexplored.

A number of other oxidizing agents were explored briefly for the epoxidation of FDNVE. Thus, 2-hydroperoxyhexafluoro-2-propanol has been shown to be a useful epoxidizing agent for acid-sensitive substrates since its reduction product, hexafluoroacetone hydrate, is a weak acid.[5] This hydroperoxide did undergo a reaction when contacted with FDNVE in CH_2Cl_2 solution with consumption of the FDNVE, but no 1 was formed. Instead, the reaction product contained much fluorodinitroethanol, and two new, unidentified products (GC analysis). Ryang and Foote[6] recently reported a new epoxidation reaction by an intermediate formed in the $Pd(OAc)_2$ catalyzed oxygenation of azibenzil. This process occurs under mild conditions and does not involve acidic or basic reactants and products. However, the intermediate generated from azibenzil did not react with FDNVE in CH_2Cl_2 under the conditions reported in the literature. Additional oxidizing agents such as molybdenyl peroxide complexes and other acyl-OOH reagents giving non-acidic reduction products:

$$C_6H_5C{\overset{=NH}{\underset{OOH}{\diagdown}}} \quad , \quad RN=C=NR + H_2O_2 \quad , \quad EtOC{\overset{=O}{\underset{OOH}{\diagdown}}} \quad ,$$
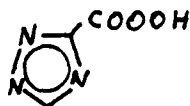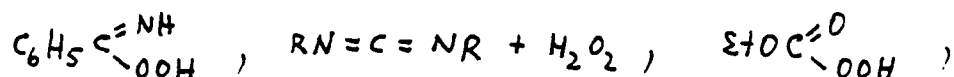
have not been tried.[7]

Another approach to the synthesis of 1 tried was the reaction of fluoro-dinitroethyl formate with diazomethane. This reaction was in analogy to the reported[8] conversion of an α-nitroester into an oxirane with diazoethane. However, in the case investigated here, no reaction took place. When BF₃ etherate was added, the diazomethane decomposed.

$$CF(NO_2)_2CH_2O-CHO \quad + \quad CH_2N_2 \quad \longrightarrow \quad \text{no reaction}$$
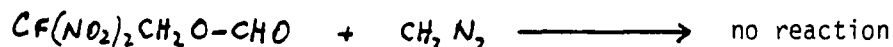
Even the still more negatively substituted fluorodinitroethyl trifluoro-acetate did not react significantly with diazomethane.

Nitro-Substituted Caprolactones

Since caprolactone is polymerized anionically, it was expected that the introduction of nitrosubstituents would facilitate polymerization. This is in contrast to cationically polymerizing monomers which are generally retarded by electron-withdrawing substituents. Therefore, the synthesis of nitrocaprolactones was attempted.

Fluorodinitromethane was added to cyclohexenone in aqueous solution in 70% yield, and the resulting 3-fluorodinitromethylcyclohexanone (2) reacted with MCPBA in refluxing CH_2Cl_2 to give 3-fluorodinitromethyl caprolactone (3) in >90% yield.
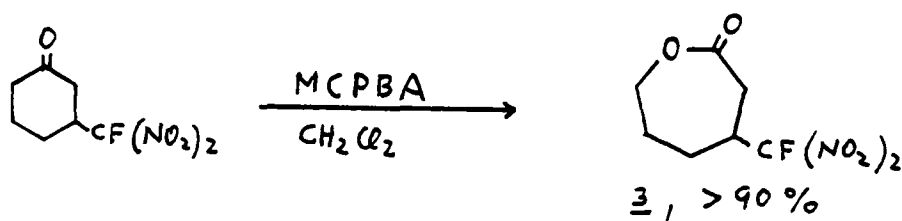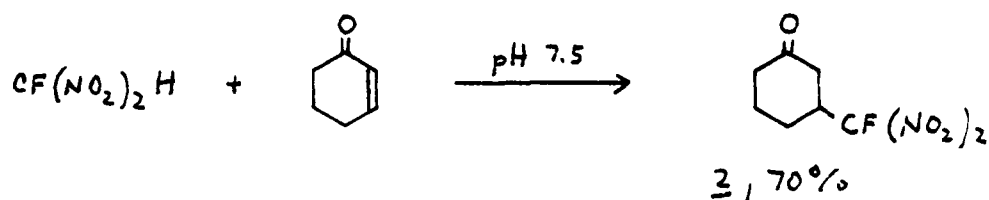
Polymerization studies with this monomer have not been carried out as yet.

Work was also begun on the synthesis of 4,4-dinitrocaprolactone (4) by the reactions of divinylketone with sodium dinitromethane and of cyclohexanedione mono-oxime with N_2O_4 to give 4,4-dinitro cyclohexanone, followed by peracid oxidation to 4.
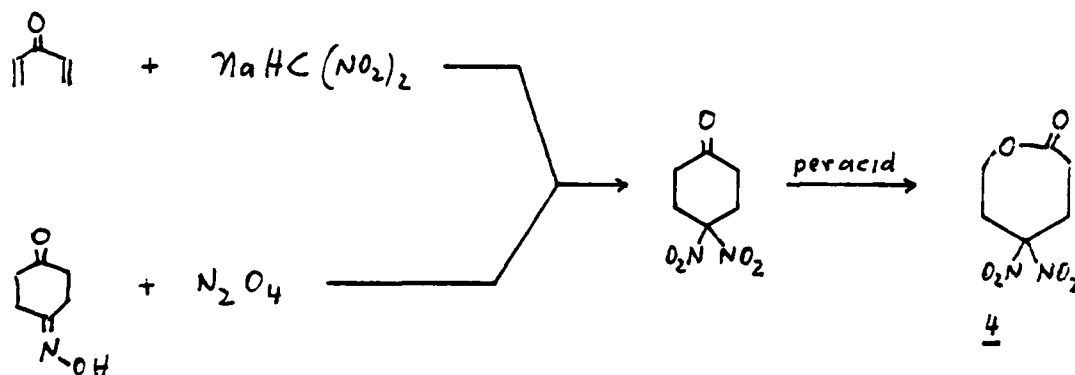
Preliminary evidence was obtained for the formation of 4,4-dinitrocyclohexanone via the divinyl ketone route. This effort was not completed due to shift of emphasis towards polyformals (see below).

Glycidyl bis(fluorodinitroethyl)amine
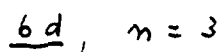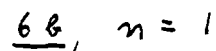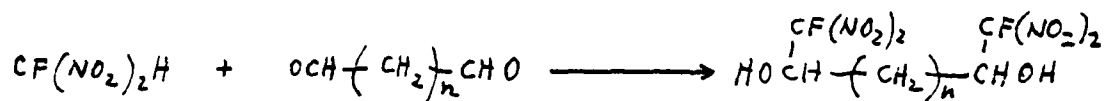
Allyl bis(fluorodinitroethyl)amine[9] reacted readily with MCPBA at elevated temperature in CHCl$_3$ solution to give on work-up a viscous oil which has tentatively been identified as the glycidyl amine $\underline{5}$. However, purification and characterization of this compound is at present incomplete.

$$\left[CF(NO_2)_2\, CH_2 \right]_2 N-CH_2\, CH=CH_2 \quad \xrightarrow[CHCl_3]{MCPBA}$$

$$\left[CF(NO_2)_2\, CH_2 \right]_2 N-CH_2\, \overset{\displaystyle O}{\overbrace{CH-CH_2}}$$

$$\underline{5}$$
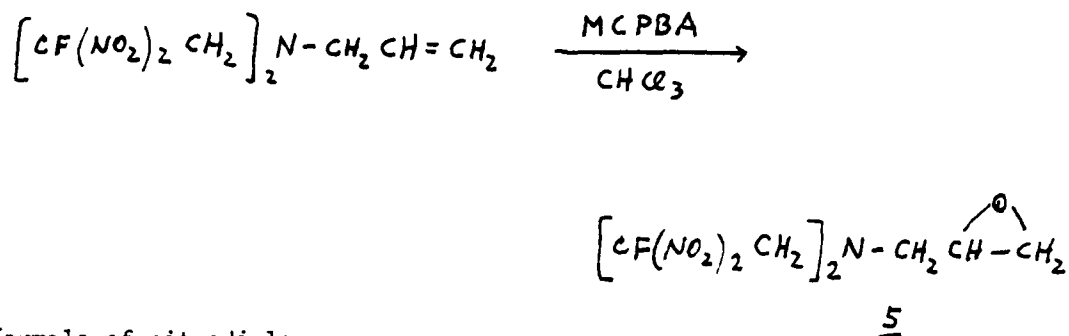
Formals of nitrodiols

The formal moiety is a well known linkage group for alcohols and has been used with great success for the preparation of valuable plasticizers and other energetic binder ingredients from polynitroalcohols.[10] Attempts have also been made to prepare polyformals derived from 2,2-dinitropropane-1,3-diol (A-diol) and from 2,2,8,8-tetranitro-4,6-dioxanonane-1,9-diol (DINOL) but have apparently not been successful because of preferred formation of the cyclic formal, 5,5-dinitro-1,3-dioxane from both precursors under the strongly acidic reaction conditions required. However, the preparation of formals from other nitrodiols, especially ones that could not form 5- or 6-membered rings, has not been reported. It was thought that such diols might form polyformals more readily than A-diol or DINOL.

The diols $\underline{6a}$-$\underline{6d}$ were prepared by us several years ago by addition of fluorodinitromethane (FDM) to the corresponding dialdehydes.[11] Except for $\underline{6a}$, mixtures of both diastereomers are obtained in all cases.

$$CF(NO_2)_2 H \;+\; OCH \overbrace{\left(CH_2 \right)_n} CHO \;\longrightarrow\; HO\overset{CF(NO_2)_2}{\underset{}{CH}} \overbrace{\left(CH_2 \right)_n} \overset{CF(NO_2)_2}{\underset{}{CH}} OH$$

$$\underline{6a},\quad n = 0$$
$$\underline{6b},\quad n = 1$$
$$\underline{6c},\quad n = 2$$
$$\underline{6d},\quad n = 3$$

We have now investigated the reaction of 6a - 6d with formaldehyde and strong acids. Alcohol 6a is unreactive under the usual conditions of formal formation from polynitroalcohols[10], i.e., paraformaldehyde/conc. H_2SO_4. This could be due in part to the poor solubility of 6a in this medium. Since the 6a obtained from the FDM addition to glyoxal is the meso isomer[12], the fluorodinitromethyl groups would be cis in the 5-membered ring formal and its formation should be sterically impeded or impossible. Thus, the formation of a polyformal could be expected. However, when the reaction was forced - CF_3SO_3H solvent, 60°C - the trioxaheptane 7 was obtained instead. This compound is a liquid and may be of interest as a plasticizer. The stability of the trioxepine structure under the highly acidic conditions is noteworthy.

6a $\xrightarrow[\text{60°C}]{CH_2O \ / \ CF_3SO_3H}$
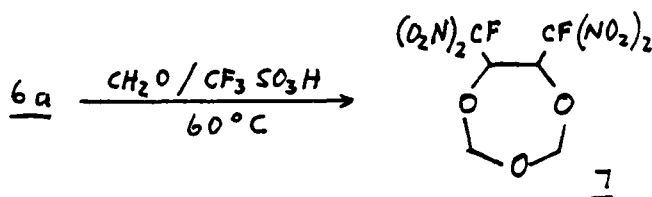
Not suprisingly, 6b reacted readily with CH_2O/H_2SO_4 to the cyclic formal 8 in excellent yield. A mixture of stercoisomers corresponding to the composition of the starting material is obtained.
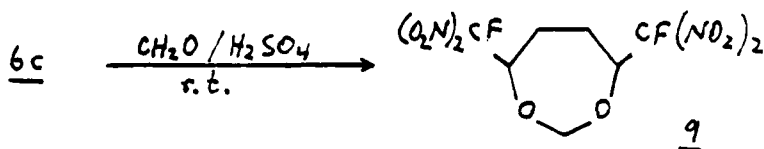
6b $\xrightarrow[\text{r.t.}]{CH_2O/H_2SO_4}$
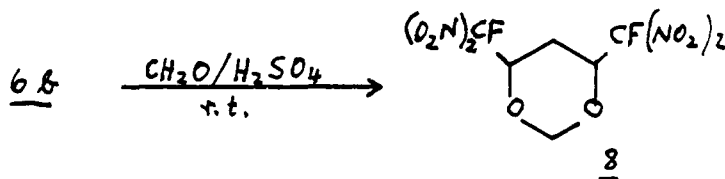
When 6c was reacted in a similar fashion, the cyclic formal 9 was obtained in almost quantitative yield.

6c $\xrightarrow[\text{r.t.}]{CH_2O \ / \ H_2SO_4}$

A minor by-product detected by TLC is thought to be the 14-membered ring dimer, but this has not been fully established. When the reaction with paraformaldehyde was run in 15% oleum, no product was obtained. In CF_3SO_3H, 9 was formed as the major product, but in low yield (ca. 30%). 9 is very stable and several attempts to polymerize it by treatment with acid catalysts were fruitless. Thus, heating

with a catalytic amount of H_2SO_4 in $ClCH_2CH_2Cl$ solution gave a small quantity
of the by-product mentioned above (TLC analysis), but no polymer. Treatment of
9 with PF_5 in CH_2Cl_2 at room temperature, elevated temperature, and at low
temperature[13] had no effect.

Finally, when 6d was reacted with CH_2O/H_2SO_4 under the usual conditions,
the major product (ca. 70% yield) was the cyclic formal 10. Several minor
by-products as well as origin material were observed by TLC analysis. As with
6c no product was obtained in 15% oleum. A run in which a solution of para-
formaldehyde in conc. H_2SO_4 was added slowly to

$$6d \xrightarrow[\text{r.t.}]{CH_2O/H_2SO_4} \quad \underset{10}{(O_2N)_2CF \diagdown O \diagdown O \diagup CF(NO_2)_2}$$
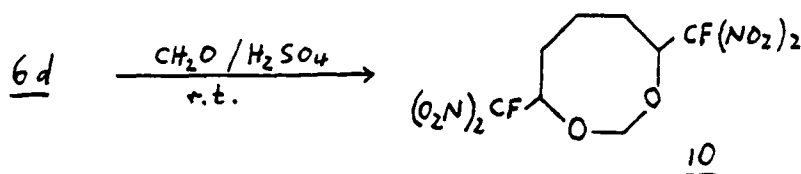
the conc. acid solution of 6d gave 10 as the sole product in 67% yield. When
the diol was dissolved in CH_2Cl_2 and treated with paraformaldehyde and only a
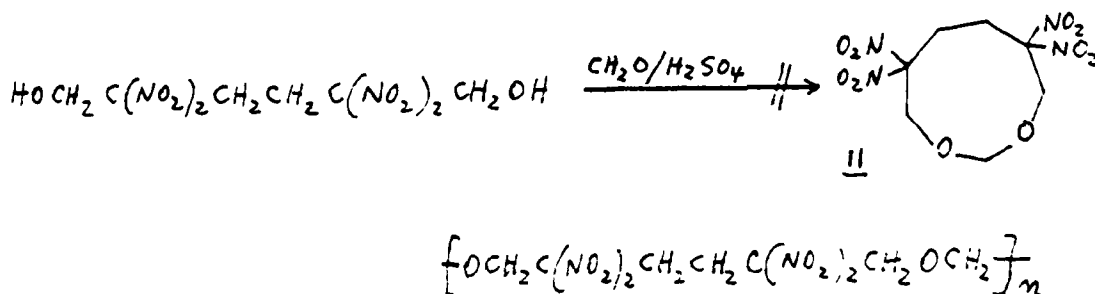small quantity of sulfuric acid, the result was the same (see below for a
different result with $BrCH_2CH(OH)CF(NO_2)_2$).

The ring of 10 is more easily cleaved than that of 9. Thus when 10 was
heated in $ClCH_2CH_2Cl$ with a catalytic amount of CF_3SO_3H at 90°C, an insoluble
polymeric material was formed, albeit in low conversion. The extent of this
polymerization varied in several repeating trials. PF_5 in CH_2Cl_2 under the
same conditions as above (6c) had no effect. With $H_2SO_4/HOAc$, 10 was cleaved
to a mixture of unidentified acetates and 6d. Treatment with CF_3SO_3H in
sulfolane gave partial cleavage to 6d.

The above results suggest that the stability of the ring decreases from
9 to 10. This is in accordance with literature reports[14] which indicate a
further reduction of thermodynamic stability for the 9-membered ring. Also,
literature reports on substituent effects on ring-opening polymerization
indicate that bulky substituents often favor ring over open chain structures.
In order to test these effects in the case of nitrodiols, 2,2,5,5-tetranitro-
hexanediol[15] was reacted with CH_2O/H_2SO_4. The product was essentially completely
insoluble in CH_2Cl_2 which rules out the presence of the 9-membered ring formal 11.
The material is completely soluble in THF and GPC analysis of this solution
indicated that a mixture of oligomers of 11 was at hand. The molecular weights
estimated from the GPC are in the range 1,500-2,500.

$$HOCH_2C(NO_2)_2CH_2CH_2C(NO_2)_2CH_2OH \xrightarrow{CH_2O/H_2SO_4} \underset{11}{11}$$

$$\{OCH_2C(NO_2)_2CH_2CH_2C(NO_2)_2CH_2OCH_2\}_n$$

3

No efforts to optimize this reaction or further characterize the product have been made. However, in view of this result future efforts will be directed at the preparation of formals from nitrohexane- or heptanediols in which one or both of the fluorodinitromethyl groups present in 6a-6d bave been replaced by a dinitromethylene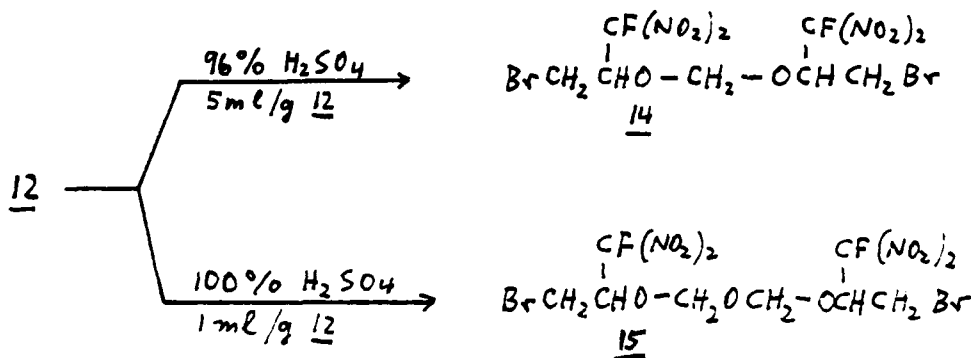 function such as present in the tetranitrohexanediol. The polyformal from the tetranitrohexanediol itself should be of interest as well.

In order to learn more about the formation of linear formals of 1-substituted fluorodinitroethanols, which had not been previously reported, the preparation of some monomeric model compounds was tried. The alcohols 12 and 13 were obtained in good yields by addition cf FDM to the corresponding aldehydes.

$$BrCH_2CHO + CF(NO_2)_2H \longrightarrow BrCH_2\underset{\underset{12}{|}}{\overset{\overset{CF(NO_2)_2}{|}}{C}}HOH$$

$$C(NO_2)_3CH_2CH_2CHO + CF(NO_2)_2H \longrightarrow C(NO_2)_3CH_2CH_2\underset{\underset{13}{|}}{\overset{\overset{CF(NO_2)_2}{|}}{C}}HOH$$
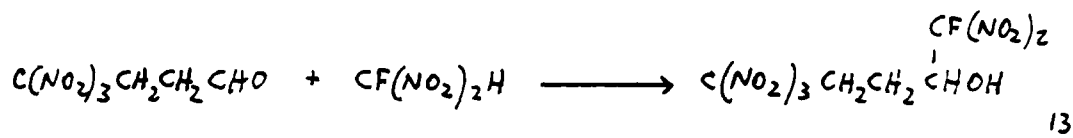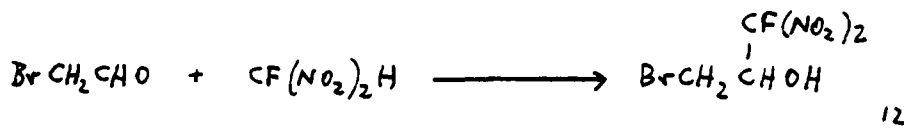
So far, only the reaction of 12 with paraformaldehyde and acid has been studied in some detail. It was found that the formal 14 is formed under the usual conditions, but only in low yield (ca. 25%). Some 12 is recovered but 50% of the starting material is not accounted for. At lower temperature the result was the same but at 50°C no 14 was obtained. Similarly, with 100% H_2SO_4 and with CF_3SO_3H little or no formal was formed. Reducing the amount or the strength of the H_2SO_4 did not improve the yield of 14; instead a second product appeared which becomes the only product with still lesser amounts of H_2SO_4. This material is the oxymethylene homolog 15.

$$12 \begin{cases} \xrightarrow[\text{5ml/g } 12]{96\% \ H_2SO_4} & BrCH_2\overset{\overset{CF(NO_2)_2}{|}}{C}HO-CH_2-O\overset{\overset{CF(NO_2)_2}{|}}{C}HCH_2Br \quad \underline{14} \\[2em] \xrightarrow[\text{1ml/g } 12]{100\% \ H_2SO_4} & BrCH_2\overset{\overset{CF(NO_2)_2}{|}}{C}HO-CH_2OCH_2-O\overset{\overset{CF(NO_2)_2}{|}}{C}HCH_2Br \quad \underline{15} \end{cases}$$

These results may indicate that the formation of linear formals of 1-substituted fluorodinitroethanols occurs much less readily than that of the cyclic formals from 6b-6d. The reasons for this are not yet clear, but the implication is clearly that future efforts should be directed to formals derived from diols with at least one primary hydroxy group.

9

Plans

1. As already indicated, a number of diols will be synthesized which can give formals of ringsize 9±1, containing no more than one fluorodinitromethyl substituent. Representative structures are as follows:

$$\underset{\displaystyle HOCH_2 \, C(NO_2)_2 \, CH_2 O CH_2 \, \overset{\displaystyle \overset{CF(NO_2)_2}{|}}{CHOH}}{}$$

$$HOCH_2 \, C(NO_2)_2 \, CH_2 \, O \, CH_2 \, C(NO_2)_2 \, CH_2 OH$$

$$HOCH_2 C(NO_2)_2 \, CH_2 CH_2 \, CH\left(CF(NO_2)_2\right) OH$$
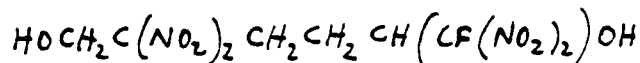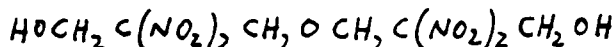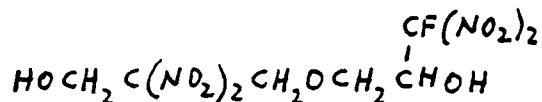
Also prepared will be a butanediol having no fluorodinitromethyl groups,

$$HOCH_2 \, C(NO_2)_2 \, CH_2 CH_2 OH$$

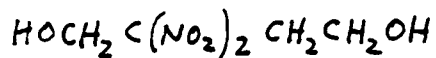and a hexanediol with 2 fluorodinitromethyl groups:
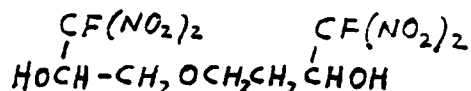
$$\underset{\displaystyle HOCH-CH_2 OCH_2CH_2 \, CHOH}{\overset{\displaystyle \overset{CF(NO_2)_2}{|} \qquad \overset{CF(NO_2)_2}{|}}{}} \qquad \text{or the all—C analog}$$

2. Formal formation will be studied for these diols and also for 2,2,5,5-tetra-nitrohexanediol. This should permit a conclusive elucidation of ringsize and substituent effects on this reaction for polynitrodiols.

3. Polymers formed will be characterized by GPC.

4. Optimization of polymer formation and preliminary evaluation will be conducted to the extent that project funds permit.

5. The work on the synthesis of nitrocaprolactones and glycidyl bis(fluoro-dinitroethyl)amine will be completed.

Experimental

General

See reference 11 for precautions in working with fluorodinitromethane and other fluorodinitro compounds. Melting points are uncorrected. Microanalyses are by Galbraith Labs., Knoxville, Tenn. Nmr spectra were obtained in part by Biomeasure, Inc. ,Hopkinton, MA, and in part on the NSWC/WO Varian XL-200 spectrometer; chemical shifts are in ppm rel. to TMS as internal standard.

Oxidation of FDNVE

To a solution of 3.6 g FDNVE[1] in 50 ml carbon tetrachloride was added in portions 4.1 g MCPBA (purity ca. 85%). The mixture was stirred for 22 h, then a few drops of Na_2SO_3 solution were added to reduce unreacted MCPBA (KI test), and the mixture was filtered. 2.85 g MCBA was recovered. The filtrate was washed twice with a pH 7 buffer solution, was dried ($MgSO_4$), and freed from solvent in vacuo to give 4.0 g of an oil which was analyzed by GC/MS as described on p. 3. In another run employing the same quantities of FDNVE and MCPBA, 30 ml hexane was used as reaction medium. After stirring the mixture overnight, the solution was decanted, the gummi solid was triturated with CH_2Cl_2, and the mixture stirred with water to which $NaHCO_3$ and $NaHSO_3$ solution was added until the KI test was negative and the pH remained >7. After separation of the phases, the organic phase was dried ($MgSO_4$) and freed from solvent in vacuo. The residual oil gave an ir spectrum very similar to that from the above CCl_4 product. The combined oils from both runs were dissolved in CH_2Cl_2 and exhaustively extracted with 0.02N, and once with 0.1 N NaOH. After drying and removing volatiles, 2.5 g of a highly viscous oil remained. The ir spectrum showed strong peaks near 1600 and 1300 cm^{-1} and a medium to weak absorption near 1740 cm^{-1}. This indicates that the material is probably a polymer of 1 containing some $m-Cl-C_6H_4COO$ groups.

Reaction of FDNVE with $(CF_3)_2CH(OH)OOH$

8.3 g of hexafluoroacetone was condensed onto 1.7 g 90% H_2O_2, and the excess allowed to evaporate. The residue was dissolved in 100 ml CH_2Cl_2. 25 ml of this solution was added to 1.8 g FDNVE and the mixture stirred 72 h at ambient temperature. The solution was dried and freed from solvent and the residue analyzed by GC; the products found were fluorodinitroethanol (major) and 2 unidentified components of higher retention times.

Reaction of FDNVE with Azibenzil/O_2

Oxygen gas was bubbled into a solution of 1.8 g FDNVE, 2.2 g azibenzil, and 0.025 g $Pd(OAc)_2$ in 25 ml CH_2Cl_2 for 24 h. GC analysis indicated no change in the FDNVE concentration while the azibenzil was completely decomposed.

3-Fluorodinitromethyl cyclohexanone, 2

A mixture of 10 ml CH_2Cl_2, 75 ml pH 7.5 buffer, 5 g cyclohexenone, and 6.25 g fluorodinitromethane was stirred 16 h at room temperature. The solid product was dissolved in additional CH_2Cl_2, the solution dried, concentrated and chilled to give 7.9 g, 70.2%, mp. 94-95°C. Nmr ($CDCl_3$): δ3.53 (m,CFCH,1), ca. 2.4 (m,5), ca. 1.8 (m,3). Anal. Calc'd for $C_7H_8FN_2O_5$: C, 38.36; H, 3.65; N, 12.79; F, 8.68. Found: C, 38.24; H, 4.17; N, 12.62; F, 8.54.

4-Fluorodinitromethyloxepanone-2, 3

A mixture of 1.1 g 2, 1.08 g m-chloroperbenzoic (ca. 85% active), and 15 ml CH_2Cl_2 was refluxed for 48 h. The mixture was then stirred with $NaHCO_3$ solution to which $NaHSO_3$ was added slowly until a negative KI test was obtained. The organic phase was washed with water, dried, and freed from solvent to give 1.05 g (90%) crude 3. After recrystallization from CH_2Cl_2/hexane, 3 had mp. 122-123°C. Nmr ($CDCl_3$): δ4.3 (m) 3.5 (m, CFCH), 2.7 (m), 1.9 (m). Anal. Calc'd for $C_7H_8FN_2O_6$: C, 35.74; H, 3.40; N, 11.91; F, 8.09. Found: C, 35.76; H, 3.86; N, 11.88; F, 8.05.

Glycidyl bis(fluorodinitroethyl)amine, 5

3.3 g crude allyl bis(fluorodinitroethyl)amine[9], 2.0 g m-chloroperbenzoic acid (ca. 85% active), and 15 ml CHCl$_3$ were refluxed for 48 h. The cooled solution was filtered, washed with dil. NaHCO$_3$ solution, dried and freed from solvent to give a viscous oil. TLC analysis showed a major product in addition to origin material, and the absence of starting material. Similarly, the methine protons (δ5.84, 5.15) of the starting material were absent from the otherwise complex Nmr spectrum. The ir spectrum had a band at 1250 cm^{-1} which is attributable to the epoxide group.

6,7-Bis(fluorodinitromethyl)trioxepane, 7

0.75 g of 6a[11] was added to a solution of 0.075 g paraformaldehyde in 5 ml CF$_3$SO$_3$H and the mixture heated at 60°C for 20 h. After drowning on crushed ice and extracting with CH$_2$Cl$_2$, the CH$_2$Cl$_2$ solution was washed with NaHCO$_3$ solution, dried (MgSO$_4$), and freed from solvent in vacuo to give 0.4 g (45%) of a mobile oil which was >95% pure by GC analysis. Nmr (CD$_2$Cl$_2$): δ5.90 (m, 2, CF(NO$_2$)$_2$CH), δ5.45, 5.30, 5.19 (4+CHDCl$_2$, OCH$_2$O). Anal. Calc'd for C$_6$H$_6$F$_2$N$_4$O$_{11}$: C, 25.81; H, 1.62; F, 10.21; N, 15.06. Found: C, 25.50; H, 1.91; F, 10.48; N, 14.75.

General procedure for preparation of 8, 9, 10

0.5 mmol diol was added to a cooled and stirred solution of 0.28 mmol trioxane or p-formaldehyde in 15 ml conc. sulfuric acid. Stirring was continued for 16 h, the mixture was poured over crushed ice and the product extracted into CH$_2$Cl$_2$. This solution was analyzed by TLC. Pure product was isolated by washing the CH$_2$Cl$_2$ solution with NaHCO$_3$ solution, drying, adding hexane, and chilling.

8: not yet characterized.

9: mp 100-125°C; Nmr (CDCl$_3$): δ5.2 (m, CFCH), 4.8 (5, OCH$_2$O), 2.17 (m), 1.94 (m). Anal. Calc'd for C$_7$H$_8$F$_2$N$_4$O$_{10}$: C, 24,29; H, 2.33; F, 10.98; N, 16.19. Found: C, 24.35; H, 2.40; F, 11.05; N, 15.97.
Also prepared was a single diastereomer of 9 from one of the diastereomers of 6c. This material was submitted to NRL for determination of the crystal structure. The crystal structure confirms the chemical structure assigned to 9.[16]

10: TLC analysis showed the presence of one major component near the solvent front in addition to several minor spots and origin material. A pure sample of 10 was obtained by filtration of a CH$_2$Cl$_2$ solution through a column of silica and collection of the initial material zone. Nmr (CDCl3): δ1.9 (m); 4.7 (d); 4.8 (s); 5.1 (d); 5.2 (t). Anal. Calc'd for C$_8$H$_{10}$F$_2$N$_4$O$_{10}$: C, 26.67; H, 2.80; F, 10.55; N, 15.56. Found: C, 27.00; H, 2.95; F, 10.80; N, 15.36.

Attempted Polymerization of 10 with CF$_3$SO$_3$H

To a solution of 1g 10 in 5 ml ClCH$_2$CH$_2$Cl was added 1 drop CF$_3$SO$_3$H, and the mixture was stirred and heated at 90°C for 2 days. After cooling, the mixture was washed with water and dried. TLC analysis indicated the presence of a significant amount of origin material. Addition of hexane to the cloud point and refrigeration gave 0.2 g solid. This was dissolved in THF and analyzed by GPC with 10 and polystyrene used as m. w. calibration standard. The m. w. range found was considerably above that of 10 with the maximum estimated at ca. 3,000.

2,2,5,5-Tetranitrohexane-1,6-diol and CH_2O/H_2SO_4

A 0.5 g sample of tetranitrohexanediol was added to a stirred solution of 0.05 g paraformaldehyde in 3 ml 90% H_2SO_4, the mixture stirred at room temperature for 4 h, and poured over crushed ice. The precipitate was filtered off (0.25 g, air-dried) and digested with CH_2Cl_2. Only 0.03 g was soluble. This indicates the absence of any significant amount of cyclic formal which is expected to be soluble in CH_2Cl_2. The CH_2Cl_2 insoluble solid was dissolved in THF and analyzed by GPC. The m. w. range present was fairly low (ca. 1,500-2,500).

1-Fluoro-1,1-dinitro-3-bromo-propanol-2, 12

A mixture of 9 g bromoacetaldehyde diethylacetal, 40 ml water, 10 ml MeOH, and 5 ml 2N H_2SO_4 was stirred at 70°C until it became homogeneous. The solution was cooled to <10°C and 5.7 g fluorodinitromethane was added, and the pH adjusted to ca. 7 with $NaHCO_3$ solution. After several h stirring with ice cooling, the mixture was acidified, saturated with NaCl and extracted 3x with CH_2Cl_2. The dried extracts were freed from solvent to give 11.0 g (96%) crude 12. TLC analysis showed the presence of only one component. A fraction was purified by chromatography on Silica and had the same ir spectrum as the crude product.

1-Fluoro-1,1,5,5,5-pentanitropentanol-2, 13

A mixture of 2.07 g 4,4,4-trinitrobutyraldehyde and 15 ml pH 7 buffer was cooled in an ice bath, 1.25 g fluorodinitromethane was added and the mixture stirred for 4 h with continued cooling. After acidification the mixture was extracted with CH_2Cl_2, the extracts dried and freed from solvent to give 3.0 g crude 13. The ir spectrum showed strong OH absorption, but also some residual C=O. The compound has not yet been completely characterized.

1-Fluoro-1,1-dinitro-3-bromopropyl-(2)-formal, 14

2.5 g 12 was added to a solution of 0.15 g paraformaldehyde in 7.5 ml conc. H_2SO_4, the mixture stirred 3 h at room temperature, then poured on crushed ice and the product extracted into CH_2Cl_2. The extract was washed with $NaHCO_3$ solution and worked up as usual to give 1.3 g of an oil which by TLC analysis was a mixture of 12 and 14. The 2 components were readily separated by chromatography on Silica and pure 14 was obtained as a pale yellow oil. Nmr ($CDCl_3$) δ3.54 (m, $BrCH_2CH$); 5.11 (d, OCH_2O); 5.2(m, CF-CH). Anal. Calc'd for $C_7H_8F_2Br_2N_4O_{10}$: C, 16.61; H, 1.59; F, 7.51; Br, 31.58; N, 11.07. Found: C, 16.40; H, 1.71; Br, 31.85; N, 10.80.

1-Fluoro-1,1-dinitro-3-bromopropoxy-(2)-methyl ether, 15

When the above reaction was conducted with 2 ml 100% H_2SO_4 for 1 h and worked up in a similar manner, 1.5 g of an oil was obtained which by LC analysis contained little 12 or 14. The main product was obtained fairly pure by chromatography on Silica. The Nmr spectrum is compatible with structure 15. Nmr ($CDCl_3$): δ3.48 (m, $BrCH_2CH$, 4); 4.86 (m, OCH_2OCH_2O, 4); 5.21 (m, $CFCH$, 2).

REFERENCES

1. H. G. Adolph, U. S. 3,808,182 (1974).

2. C. L. Stevens and S. J. Dykstra, JACS 75, 5975 (1953).

3. C. L Stevens and J. Tazuma, JACS 76, 715 (1954); C. L. Stevens and J. J. DeYoung, ibid. 718.

4. B. S. Gorton and J. A. Reeder, J. Org. Chem. 27, 2920 (1962).

5. R. P. Heegs and B. Ganem, JACS 101, 2484 (1979).

6. Hong-Son Ryang and C. S. Foote, JACS 102, 2129 (1980).

7. For leading references, see B. Plesnicar in "Oxidation in Organic Chemistry," W. S. Trahanovsky Ed., p. 255, Acad. Press, New York (1978).

8. F. M. Dean and B. K. Park, Chem. Comm. 1974, 162.

9. V. Grakauskas and K. Baum, J. Org. Chem. 36, 2599 (1971).

10. K. G. Shipp and M. E. Hill, J. Org. Chem. 31 (1966); T. N. Hall and K. G. Shipp, U. S. 3,288,863 (1966).

11. H. G. Adolph, J. Org. Chem. 35, 3188 (1970).

12. Ch. Dickinson and J. R. Holden, Acta Cryst. B35, 487 (1979).

13. This was done because of the low ceiling temperatures observed in many ring-opening polymerizations; see K. J. Ivin in "Reactivity, Mechanism, and Structure in Polymer Chemistry," A. D. Jenkins and A. Ledwith Ed., pp.514-519, Wiley & Sons (1974).

14. A. Greenberg and J. F. Liebman, Strained Organic Molecules, p. 66, Acad. Press, New York (1978).

15. H. Feuer, C. E. Colwell, G. Leston, and A. T. Nielsen, J. Org. Chem. 27, 3598 (1962).

16. R. Gilardi, NRL, private communication.

ENERGETIC MATERIALS RESEARCH

DISTRIBUTION LIST

	Copies		Copies
Assistant Secretary of the Navy (R, E, and S) Attn: Dr. R. E. Reichenbach Pentagon Washington, DC 20350	1	Defense Technical Information Center DTIC-DDA-2 Cameron Station Alexandria, VA 22314	12
Office of Naval Research Attn: Dr. R. Miller Code 473 Arlington, VA 22217	10	AFATL Attn: Dr. Otto K. Heiney Eglin AFB, FL 32542	1
Office of Naval Research Attn: Dr. J. Enig Code 200B Arlington, VA 22217	1	AFRPL Attn: Mr. W. C. Andrepont Code PACC Edwards AFB, CA 93523	1
Office of Naval Research Attn: Mr. D. Siegel Code 260 Arlington, VA 22217	1	AFRPL Attn: Dr. R. R. Weiss Code CA Edwards AFB, CA 93523	1
Office of Naval Research Western Office Attn: Dr. T. Hall 1030 East Green Street Pasadena, CA 91106	1	Code AFRPL MKPA Attn: Mr. R. Geisler Edwards AFB, CA 93523	1
		Code AFRPL MKPA Attn: Dr. F. Roberto Edwards AFB, CA 93523	1
Office of Naval Research Eastern Central Regional Office Attn: Dr. L. Peebles Dr. A. Wood 495 Summer Street Boston, MA 02210	1 1	AFSC Attn: Mr. Richard Smith Andrews AFB, Code DLFP Washington, DC 20334	1
Office of Naval Research Attn: Dr. P. A. Miller San Francisco Area Office One Hallidie Plaza Suite 601 San Francisco, CA 94102	1	Air Force Office of Scientific Research Directorate of Chemical & Atmospheric Sciences Bolling Air Force Base Washington, DC 20332	1

Copies

Copies

Air Force Office of Scientific
 Research
Attn: Dr. L. H. Caveny   1
Directorate of Aerospace
 Sciences
Bolling Air Force Base
Washington, DC   20332

Anal-Syn Lab Inc.
Attn: Dr. V. J. Keenan   1
P. O. Box 547
Paoli, PA   19301

Army Ballistic Research Labs
Attn: Mr. L. A. Watermeier   1
Code DRDAR-BLP
Aberdeen Proving Ground, MD   21005

Army Ballistic Research Labs
ARRADCOM
Attn: Dr. Ingo W. May   1
Code DRDAR-BLP
Aberdeen Proving Ground, MD   21005

Army Ballistic Research Labs
ARRADCOM
Attn: Dr. Philip Howe   1
Code DRDAR-BLP
Aberdeen Proving Ground, MD   21005

Army Missile Command
Attn: Dr. R. G. Rhoades   1
      Dr. W. W. Wharton   1
Code DRSME-RK
Redstone Arsenal, AL   35809

Atlantic Research Corp.
Attn: Dr. C. B. Henderson   1
5390 Cherokee Avenue
Alexandria, VA   22314

Ballistic Missile Defense
 Advanced Technology Center
Attn: Dr. David C. Sayles   1
P. O. Box 1500
Huntsville, AL   35807

Ballistic Research Laboratory
Attn: Dr. A. W. Barrows   1
USA ARRADCOM
DRDAR-BLP
Aberdeen Proving Ground, MD   21005

Hercules Inc. Cumberland
Attn: Dr. Rocco Musso   2
Aerospace Division Allegany
 Ballistics Lab
P. O. Box 210
Cumberland, MD   21502

Hercules Inc. Eglin
Attn: Dr. Ronald L. Simmons   1
AFATL/DLDL
Elign AFB, FL   32542

Hercules Inc. Magna
Attn: Mr. E. H. DeButts   1
Bacchus Works
P. O. Box 98
Magna, UT   84044

Hercules Inc. Magna
Attn: Dr. James H. Thacher   1
Bacchus Works
P. O. Box 98
Magna, UT   84044

HQ US Army Material Development
 Readiness Command
Attn: Mr. S. R. Matos   1
Code DRCDE-DW
5011 Eisenhower Avenue
Room 8N42
Alexandria, VA   22333

Johns Hopkins University APL
Attn: Mr. Theodore M. Gilliland   1
Chemical Propulsion Information
 Agency
Johns Hopkins Road
Laurel, MD   20810

16

DISTRIBUTION (Cont.)

Copies   Copies

Lawrence Livermore Laboratory
Attn: Dr. M. Finger   1
University of California
Livermore, CA 94550

Naval Ordnance Station
Attn: Mr. S. Mitchell   1
Code 5034
Indian Head, MD 20640

Lawrence Livermore Laboratory
Attn: Dr. R. McGuire   1
University of California
Livermore, CA 94550

Naval Ordnance Station
Attn: Mr. C. L. Adams   1
Code PM4
Indian Head, MD 20640

Lockheed Missiles and Space Co.
Attn: Dr. Jack Linsk
      Org. 83-10 Bldg. 154   1
P. O. Box 504
Sunnyvale, CA 94088

Dean of Research
Attn: Dr. William Tolles   1
Naval Postgraduate School
Monterey, CA 93940

Lockheed Missile and Space Co.
Attn: Dr. H. P. Marshall   1
      Dept. 52-35
3251 Hanover Street
Palo Alto, CA 94304

Naval Research Lab
Attn: Dr. J. Schnur   1
Code 6510
Washington, DC 20375

Los Alamos Scientific Lab
Attn: Dr. R. Rogers, WX-2   1
P. O. Box 1663
Los Alamos, NM 87545

Naval Research Lab
Code 6100
Washington, DC 20375   1

Los Alamos Scientific Lab
Attn: Dr. B. Craig, M Division   1
P. O. Box 1663
Los Alamos, NM 87545

Naval Sea Systems Command
Attn: Mr. G. Edwards, Code 62R3   1
      Mr. J. Murrin, Code 62R2   1
      Mr. W. Blaine, Code 62R   1
Washington, DC 20362

Naval Air Systems Command
Attn: Mr. R. Heitkotter   1
      Mr. R. Brown   1
Code 330
Washington, DC 20360

Naval Sea Systems Command
Attn: Mr. R. Beauregard, SEA 64E   1
      SEA 09G32   2
      SEA 03B   1
Washington, DC 20362

Naval Air Systems Command
Attn: Dr. H. Mueller   1
      Dr. H. Rosenwasser   1
Code 310
Washington, DC 20360

Naval Weapons Center
Attn: Dr. R. Atkins   1
Code 3853
China Lake, CA 93555

Naval Explosive Ordnance
  Disposal Facility
Attn: Lionel Dickinson (Code D)   1
Indian Head, MD 20640

Naval Weapons Center
Attn: Dr. L. Smith   1
Code 3205
China Lake, CA 93555

DISTRIBUTION (Cont.)

	Copies		Copies
Naval Weapons Center Attn: Dr. C. Thelen Code 3205 China Lake, CA 93555	1	Strategic Systems Project Office Attn: Dr. J. F. Kincaid Department of the Navy Room 901 Washington, DC 20376	1
Naval Weapons Center Attn: Dr. A. Amster Code 385 China Lake, CA 93555	1	Strategic Systems Project Office Attn: Mr. E. L. Throckmorton Mr. R. Kinert Department of the Navy Room 1048 Washington, DC 20376	1 1
Naval Weapons Center Attn: D. R. Derr Code 388 China Lake, CA 93555	1		
Naval Weapons Center Attn: Dr. R. Reed, Jr. Code 388 China Lake, CA 93555	1	Thiokol Chemical Corp. Brigham City Attn: Dr. G. Thompson Wasatch Division Brigham City, UT 84302	1
Naval Weapons Center Attn: Dr. A. Nielsen Code 385 China Lake, CA 93555	1	USA ARRADCOM Attn: Dr. R. F. Walker DSDAR-LCE Dover, NJ 07801	1
Naval Weapons Center Attn: Mr. E. Martin Code 3858 China Lake, CA 93555	1	USA ARRADCOM Attn: Dr. N. Slagg DSDAR-LCE Dover, NJ 07801	1
Naval Weapons Center Attn: Mr. R. McCarten China Lake, CA 93555	1	U.S. Army Research Office Chemistry Division P. O. Box 12211 Research Triangle Park, NC 27709	1
Naval Weapons Support Center Attn: Dr. B. Douda Code 5042 Crane, IN 47522	1	Univ. of Illinois at Chicago Circle Attn: Professor J. H. Boyer Department of Chemistry Box 4348 Chicago, IL 60680	1
Rohm and Haas Company Attn: Dr. H. Shuey 723-A Arcadia Circle Hunsville, AL 35801	1	University of Massachusetts Attn: Professor J. C. Chien Department of Chemistry Amherst, MA 03003	1

DISTRIBUTION (Cont.)

	Copies		Copies
Rockwell International Attn: Dr. M. B. Frankel Rocketdyne Division 6633 Canoga Avenue Canoga Park, CA 91304	1	University of Massachusetts Attn: Professor P. Lillya Department of Chemistry Amherst, MA 03003	1
Polysciences, Inc. Attn: Dr. B. David Halpern Paul Valley Industrial Park Warrington, PA 18976	1	Office of Naval Research Attn: Dr. G. Neece, Code 472 800 N. Quincy St. Arlington, VA 22217	1
The Johns Hopkins University Attn: Dr. Joyce J. Kaufman Department of Chemistry Baltimore, MD 21218	1	SRI International Attn: Dr. D. L. Ross 333 Ravenswood Avenue Menlo Park, CA 94025	1